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13. ABSTRACT (Maximum 200 words)

This is the Final Report of a three-year grant the goal of which was to develop an atomistic simulation approach toward the modeling of structurall, thermal and mechanical behavior of SiC fiber composites. The Report contains an Executive Summary, a description of research highlights, a list of the 26 publications which result ed from the project, a list of the participating personnel, and an appendix consisting of three extended summaries presented at the annual program reviews each of the three years.

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Atomistic Modeling of SiC Fiber Composites

submitted by

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July 5, 2000

Contents

A. Executive Summary

The overall thrust of this three-year project was to develop an atomistic simulation approach toward the modeling of structural, thermal and mechanical behavior of SiC fiber composites. On the premise that materials theory and simulation have advanced to the stage where, under favorable circumstances, quantitative analyses and predictions are now feasible, we have embarked on a task of combining the development of general simulation concepts and techniques for probing thermomechanical properties with materials-specific applications to SiC. The principal challenges in this endeavor were the complexity of the interatomic interactions intrinsic to SiC, and the complexity of defect microstructures which governs how the material behaves at elevated temperatures and stress levels.

The fundamental advantage of atomistic simulation is that once an interaction potential model for the specific material of interest is established, a variety of physical responses can be studied under well characterized environmental conditions. Given that simplifications were necessary in developing the potential model for SiC, extensive validations against experimental measurements, whenever possible, were considered an integral part of the study. Essentially all the results reported in this project have been obtained using a potential that was originally proposed in 1989. Although the description has known shortcomings, it is still considered to be the most robust and tractable model available to date.

The most significant findings from the project work are summarized in the following section on Research Highlights, while the entire research output that has been published is listed in section C. Our contributions to atomistic concepts and simulation studies ranged from thermodynamic, vibrational and transport properties to defect mobility, structural deformation and crack propagation, with applications not only to SiC, but also to a related covalent material Si. The distribution of the 26 publications among the three areas, technique development, mechanical behavior studies, and SiC-specific applications is 11, 8, and 7.

At the conclusion of the project it was felt that despite the progress that has been made, much work still remains ahead to achieve the goal of gaining fundamental understanding of the mechanisms and factors controlling the performance of ceramics at high temperatures. Building on this progress, it seemed now practical to envisage an atomistic study of strength, deformation and toughness of specific ceramic materials models at temperatures approaching their melting point, in the framework of multiscale modeling,

The remaining parts of the Report are Section D which shows the participating personnel, and an appendix consisting of the extended summaries presented at the annual review of the AFOSR Structural Ceramics and Composites program for each of the three years of the project.

B. Research Highlights

The underlying theme of the project research throughout the three-year period has been the atomic-level study through theory and simulation of the thermal and mechanical behavior of crystalline solids with covalent bonding. To summarize the significant findings from this undertaking, we classify the research results according to three areas of primary contribution, the development of atomistic concepts and simulation techniques that have rather general applicability, studies of structural stability including defects and cracks, and applications which pertain specifically to SiC. Each area is then discussed briefly with explicit reference to the corresponding publications listed in Section C.

Atomistic Modeling Concepts and Simulation Techniques

The structural and dynamical behavior of a system of interacting atoms in a thermal environment with or without external stress can be studied in detail using molecular dynamics and various relaxation and sampling techniques. We have reported results on thermodynamic properties and defect mobilities of Si [1, 2, 9, 16, 24] using the same type of interatomic interaction potential that was later extended to SiC. Comparison between simulation predictions and available experimental data provides a measure of confidence in the reliability of the Tersoff bond-order potential model. In another area of contribution, we have developed a new method for the efficient calculation of free energy involving the concepts of coupling parameter and reversible scaling [20, 23, 25]. As a result, one can perform accurate free energy determination over a wide temperature range on the basis of simulation at a single temperature. Still another contribution in the sense of coupling atomistic simulations to a surrounding continuum is the development of statistical techniques for minimizing the effects of border perturbations [21, 22].

Structural Stability and Crack Propagation

We have extended our previous derivation of elastic stability criteria to studies of melting by isobaric heating and the stress-induced onset of structural instability, where molecular dynamics simulations provide atomic-level details that are not available by other means [3]. A consequence of this work is a unified picture of how homogeneous lattices lose their mechanical stability when perturbed by thermal agitation or by external stress loading. We have also contributed to other aspects of fracture mechanics, that of dislocation nucleation at the crack tip and the subsequent strain relief [7, 11], along with the implementation of linking atomistic and continuum calculations [15]. These various results have implications for determining the material strength, in contrast to the effects grain size [14].

SiC Applications

During various stages of the project we have carried out atomistic simulation studies of beta-SiC (3C) in order to build up a database of thermal properties and mechanical behavior of this material. The former include the calculations of lattice vibration, heat capacity, thermal expansion, and thermal conductivity [4 – 6, 10], while the latter involve two different types of lattice response to external stress. One response concerns a local vibrational analysis designed to predict the breaking of an interatomic bond as a precursor to fracture initiation under tensile loading [8, 19]. The other response is the behavior under hydrostatic compression where the zinc-blende lattice undergoes a crystal to amorphous transition, a phenomenon that can be

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interpreted in terms of a competition between two shear instabilities and furthermore, the role of atomic size in chemical disorder [13, 17, 24].

Taken together, the project contributions represent a collection of material modeling concepts and atomistic simulation techniques, as well as a body of specific results on covalent solids, particularly SiC (3C), which should be of interest to the materials research community. One potentially important area of application where these findings could be useful is in the computational materials analysis and design. With the advent of high-performance computing and the progress in scientific computations and visualizations, there is increasing interest given to the role of multiscale materials modeling and simulation, with the community of materials research responding in an enthusiastic manner [18]. In this context, the work reported here serves as a first step toward realizing the goal of understanding and designing ceramic materials for high-temperature applications.

C. Project Publications

The following publications report work supported wholly or in part by the project.

1. L. J. Porter, S. Yip, M. Yamaguchi, H. Kaburaki, M. Tang, "Empirical Bond-Order Description of Thermodynamic Properties of Crystalline Silicon", Journal of Applied Physics **81**, 96 (1997).

2. V. Bulatov, M. Nastar, J. Justo, S. Yip, "Atomistic Modeling of Crystal-Defect Mobility and Interactions", Nuclear Instruments and Methods in Physics Research B **121**, 251 (1997).

3. J. Wang, J. Li, S. Yip, D. Wolf, S. Phillpot, "Unifying Two Criteria of Born: Elastic Instability and Melting and Homogeneous Crystals", Physica A **240**, 396 (1997).

4. J. Li and S. Yip, "Order-N Method to Calculate the Local Density of States", Physical Review B **56**, 3524 (1997).

5. L. J. Porter, J. Li, S. Yip, "Atomistic Modeling of Finite-Temperature Properties of Beta-SiC. I. Lattice Vibrations, heat Capacity, and Thermal Expansion", Journal of Nuclear Materials **246,** 53 (1997).

6. L. J. Porter, J. Justo, S. Yip, "The Importance of Gruneisen Parameters in Developing Interatomic Potentials", Journal of Applied Physics **82,** 5378 (1997).

7. F. Cleri, S. Yip, D. Wolf, S. R. Phillpot, "Atomic-Scale Mechanism of Crack-Tip Plasticity: Dislocation Nucleation and crack-Tip Shielding", Physical Review Letters **79**, 1309 (1997).

8. C. S. Jayanthi, M. Tang, S. Y. Wu, J. A. Cocks, S. Yip, "Local Analysis of Structural Instability in Stressed Lattices: Crack Nucleation in a Covalent Solid", Physical Review Letters **79**, 4601 (1997).

9. V. V. Bulatov, J. F. Justo, W. Cai, S. Yip, "Kink Asymmetry and Multiplicity in Dislocation Cores", Physical Review Letters **79**, 5042 (1997).

10. M. Tang and S. Yip, 'Pressure-driven elastic instabilities and solid-state amorphization", in The Physics of Complex Systems, F. Mallamace and H. E. Stanley, eds. (IOS Press, Amsterdam, 1997), p. 533.

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12. F. Cleri, S. R. Phillpot, D. Wolf, S. Yip, "A Method for the Simulation of Fracture at the Atomic Level", in Advances in Computational Materials Science, V. Fiorentini and F. Meloni, eds. (Italian Physical Society, Bologna, 1997), pp. 71-88.

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14. S. Yip, "The Strongest Size", Nature **391**, 532 (1998).

15. F. Cleri, S. R. Phillpot, D. Wolf, S. Yip, "Atomistic Simulations of Materials Fracture and the Link between Atomic and Continuum Length Scales", Journal of American Ceramic Society **81**, 501 (1998).

16. J. F. Justo, M. Z. Bazant, E. Kaxiras, V. V. Bulatov, S. Yip, "Interatomic Potential for Silicon Defects and Disordered Phases", Physical Review B **58**, 2539 (1998).

17. K. Mizushima, M. Tang, S. Yip, "Toward Multiscale Modelling: the role of atomistic simulations in the analysis of Si and SiC under hydrostatic compression", J. Alloys & Compounds **279**, 70 (1998).

18. E. Kaxiras and S. Yip, "Modelling and Simulation of Solids - Editorial Overview", Current Opinion in Solid State & Materials Science **3**, 523 (1998).

19. C. S. Jayanthi, M. Tang, S. Y. Wu, J. A,. Cocks, S. Yip, "Insights on Deformation Mechanisms from Atomistic Modeling of Structural Instability in Solids", in *Computer-Aided Design of High-Temperature Materials*, A. Pechenik, R. K. Kalia, and P. Vashishta, eds. (Oxford Univ. Press, New York, 1999), p. 55.

20. M. De Koning, A. Antonelli, S. Yip, "Optimized Free Energy Evaluation Using a Single Reversible-Scaling Simulation", Physical Review Letters **83**, 3973 (1999).

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22. J. Li, D. Liao and S. Yip, "Nearly Exact Solution for Coupled Continuum/MD Fluid Simulation", J. Computer-Aided Materials Design **6**, 95 (1999).

23. M. de Koning, A. Antonelli, S. Yip, "Reversible Scaling: Optimized Free-Energy Determination using Atomistic Simulation Techniques", J. Computer-Aided Materials Design **6**, 349 (1999).

24. J. F. Justo, V. V. Bulatov, S. Yip, "Dislocation Core Reconstruction and Its Effect on Dislocation Mobility in Silicon", Journal of Applied Physics **86**, 4249 (1999).

25. S. Yip, J. Li, M. Tang, J. Wang, "Mechanistic Aspects and Atomic-Level Consequences of Elastic Instabilities in Homogeneous Crystals", Materials Science and Engineering A (in press).

26. M. de Koning, W. Cai, A. Antonelli, S. Yip, "Efficient Free-Energy Calculations by the Simulation of Nonequilibrium Processes", Computing in Science and Engineering **2**, 88 (2000).

D. Participating Personnel

Principal Investigator:	Sidney Yip
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	Ju Li (6/1/98-7/31/99)
	Dongyi Liao (6/1/98-7/31/99)
Postdoctoral Associates:	Lisa Porter (9/1/96-1/15/97)
	Joao Justo (5/1/97-7/31/97)

ATOMISTIC MODELING OF SIC/C INTERFACES

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Abstract

We describe an atomistic approach to modeling thermomechanical responses of SiC interfaces. The aim of the project is to develop a multiscale simulation capability for understanding the mechanical behavior and fracture toughness of the composite material in terms of local structural and compositional characteristics of the interface. Initially the study focuses on building an atomistic model of SiC/X interface, where X could be SiC or C in either crystalline or amorphous form, a longer term goal is to let X be SiO_2. The effects of oxygen and carbon impurities on the microstructure and physical properties will be considered systematically. For treating the interatomic interactions, empirical potential functions will be used first, followed by an electronic-structure description in the tight-binding approximation. Once a model is judged to be sufficiently realistic, molecular dynamics simulations will be carried out to probe the mechanisms of interfacial relaxation and deformation at finite temperature and external loading. Another significant component of the research lies in linking the atomic-level simulations with mesoscale Monte Carlo or finite-element methods.

A Simulation Roadmap. The basic elements of the methodology we expect to implement are organized in Fig.1 in the form of a flow chart. In examining each of the elements in the order indicated, we will either present results or describe the approach we plan to follow. We consider monolithic SiC as the reference system and various interfaces SiC/X. Atomistic model refers to an appropriate interatomic interaction description. We have adopted an empirical bond-order potential developed by Tersoff for SiC which also can be used for pure Si and C (diamond). This is a purely covalent description which we have found to give generally satisfactory results for most of the thermomechanical properties of interest around equilibrium conditions [1]. We are also in the process of developing a tight-binding model for SiC using a database generated by first-principles ab initio calculations [2]. For SiO_2 we intend to use an empirical ionic potential in the literature which appears to be comparable in relative robustness to the Tersoff potential [3].
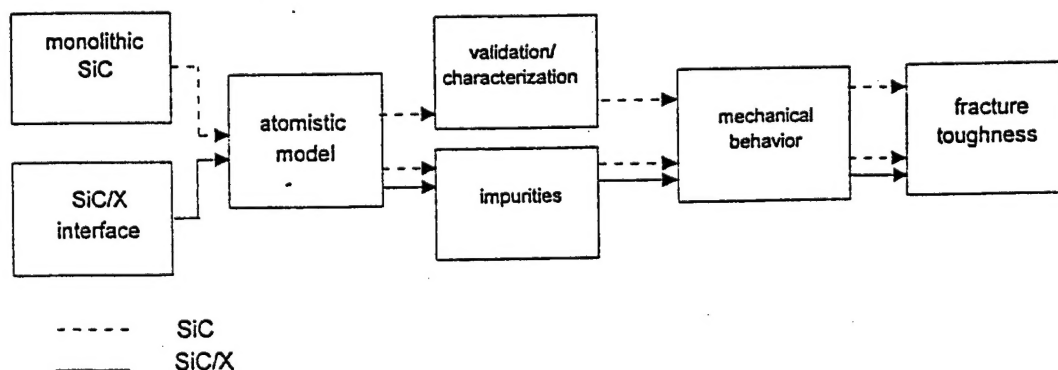

Figure 1: Simulation Roadmap showing various key elements in a multiscale modeling program on the study of mechanical strength and deformation mechanisms of SiC interfaces.

Validation/characterization refers to the calculation of the relaxed atomic structure and various basic physical properties of the atomistic model. This is the step by which one demonstrates that the model is sufficiently realistic by comparison of model-specific simulation results with experimental data. This confirmation is essential to ensure that further simulations of more complicated processes and behavior using the model are likely to be physically meaningful. In the case of monolithic $\beta - SiC$ as described by the Tersoff potential function, such results have been obtained. Below we summarize a comparison with experimental data of the lattice parameter r, cohesive energy E, and elastic constants C_{ij}, in units of Mbar [1].

	r (A)	E (eV)	B	C_{11}	C_{12}	C_{44}
Tersoff model	4.32	-6.18	2.25	4.36	1.20	2.55
Expt.	4.36	-6.34	2.25	3.90	1.42	2.56

In the course of studying these properties we have also considered two other empirical potential descriptions of SiC, an earlier model consisting of two- and three-body interactions by Pearson and co-workers in 1984 and a modified embedded-atom model proposed by Baskes in 1994. Neither model were found to be as successful.

As further indications that the Tersoff potential provides a reasonable overall description of physical properties of $\beta - SiC$, we show in Figs. 2 - 5 how the results on equation of state, vibrational and thermal properties compare with experiment. Fig. 2 shows the predicted pressure-volume curve and two sets of data [1]. Also it can be seen that both
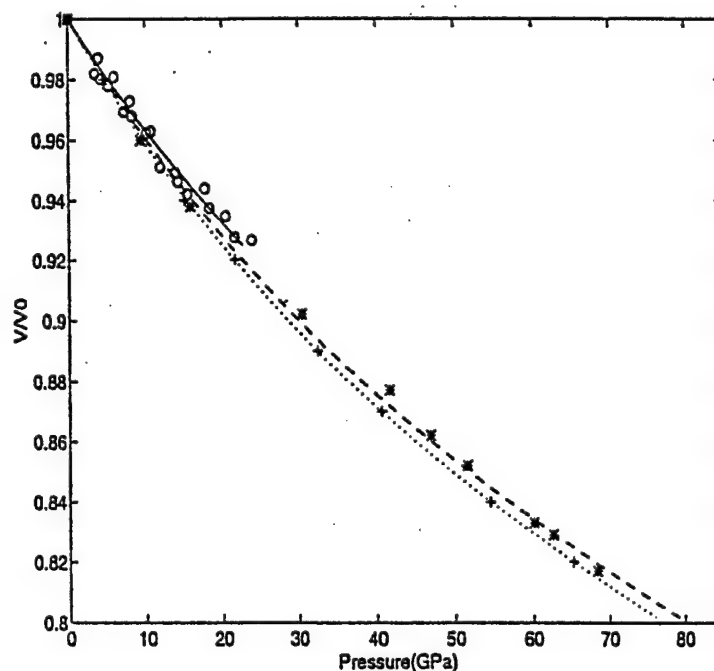

Figure 2: Pressure-volume behavior of SiC under compression at room temperature, circles and stars are experimental data, with fits to the Birch-Murnaghan equation of state denoted by dashed and chained lines respectively, while crosses are simulations using the Tersoff potential, with a similar fit shown by the solid line [1].

experiment and simulation data can be well fitted to the Birch-Murnaghan equation of state. In the the phonon dispersion curves [6], shown in Fig. 3, one sees that the potential model does not give any splitting of the optic modes because ionic interactions have been completely neglected. It is known that this effect can be captured in a tight-binding description. Heat capacity and thermal expansion coefficient are shown in Figs. 4 and 5 respectively [6]. Since molecular dynamics is a classical calculation it is necessary to take into account the effects of zero point vibration at low temperatures. The method we have adopted is one of temperature scaling [7]. Agreement of the thermal properties with experiments is quite satisfactory considering that no temperature-data were used in developing the potential model. Similar results for carbon (diamond) have been obtained with comparable or slightly better accuracy. One may thus conclude that the Tersoff potential works better the stronger the directional bonding [8].
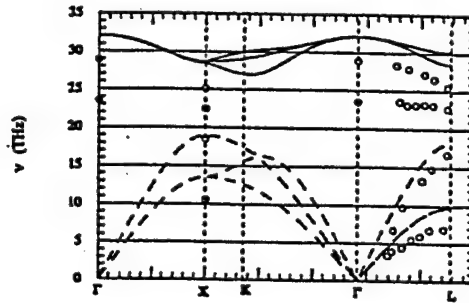

Figure 3: Phonon dispersion curves of $\beta - SiC$ at 0 K and zero pressure, solid and dashed lines indicate optic and acoustic modes respectively, and circles are experimental data [6].
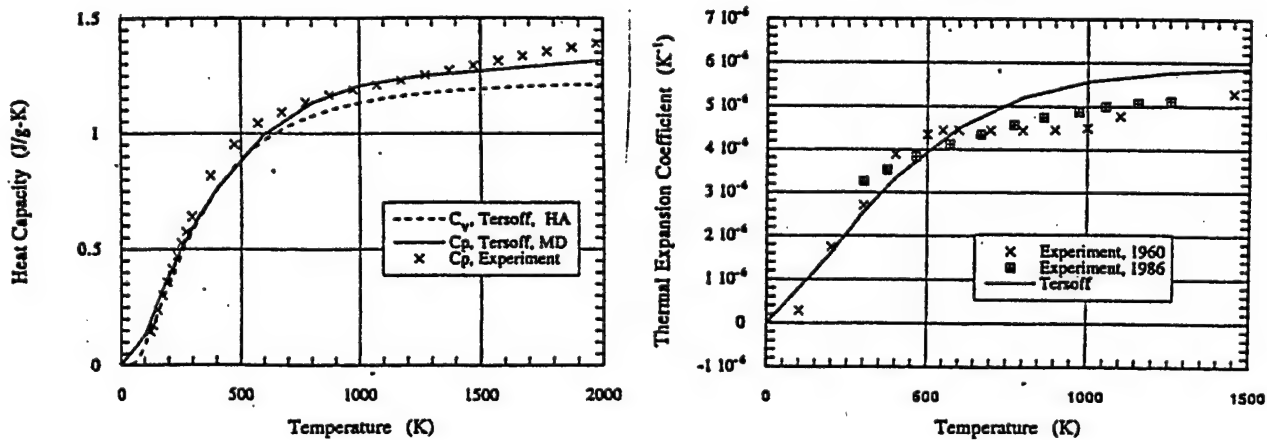

Figure 4: Heat capacity of $\beta - SiC$ obtained by molecular dynamics simulation and using the Tersoff potential, C_v and C_p are given by the dashed and solid lines respectively, and experimental data are denoted by crosses [6].

Figure 5: Thermal expansion coefficient of $\beta - SiC$, molecular dynamics results are given by the solid line while two sets of experiments are denoted by crosses and squares [6].

Impurities refers to an important aspect of the problem because concentration levels of excess carbon (stoichiometry) and oxygen impurity in the SiC component materials are sufficiently high as to have significant impact on the microstructure and physical properties. This is an area where modeling can elucidate the atomic-level mechanisms which govern impurity mobility and segregation. We have initiated a study of the effects of stoichiometry on mechanical properties using molecular dynamics and the Tersoff potential. The temperature variation of Young's modulus and shear modulus C_{44} at C/Si ratios ranging from 1.0 to 1.6 in monolithic $\beta - SiC$ have been obtained. The former shows a monotonic increase with C/Si ratio and a linear decrease with the increasing temperature. Although the latter shows more scatter, indicating better statistics are needed, one can discern a tendency to increase somewhat with C/Si ratio, and a noticeably weaker temperature dependence. We are in the process of comparing our results with experiments [4,5] which apparently are not consistent, possibly because of complicating factors associated with microstructural characterization of the samples .

The element of mechanical behavior in Fig. 1 represents a major focus of our project, the determination of materials strength and deformation behavior at elevated temperature and external loading. These are also conditions inducive of microstructural evolution. We expect that the ability to monitor simultaneously local stresses and strains will give much insight into the different modes of deformation at the SiC/X interface.

Proceeding along the SiC/X interface branch (solid line) in the flow chart in Fig. 1, we are in the process of constructing SiC/X interface models, where X can be crystalline or amorphous SiC or C (diamond). Analysis of a few early models of this type in terms of bond length and bond angle distributions suggests that the interfacial structure is roughly intermediate to that of the crystalline lattice and the amorphous material. Our plans are to focus on contrasting the microstructure and properties of the interface with those of the crystalline and amorphous reference systems.

With regard to using molecular dynamics to probe the structural response of a homogeneous lattice to a uniform external load, we have carried out a series of stability studies using potential models for fcc metals, intermetallic, and covalent solids. We have also derived a set of elastic stability criteria by formulating a Gibbs integral which combines the change in the Helmholtz free energy and the external work done during deformation, in analogy with the Gibbs free energy [9]. Several specific cases in which a cubic lattice is subjected to hydrostatic loading up to a critical strain have been analyzed, and simulation results obtained as a direct test of predictions based on the stability criteria.

In the case of bulk $\beta - SiC$ under hydrostatic tension we have observed cleavage crack nucleation at a critical stress (0.37 Mbar) in agreement with the predicted value [10]. Failure mode was found to be the vanishing of the bulk modulus, and decohesion occurs as spontaneous cracking on the {111} shuffle planes. An interesting observation was that atomic relaxation on the newly generated cracked surfaces appeared to take place immediately following crack opening. In another study of the same atomistic model but now under hydrostatic compression, we found that the homogeneous lattice undergoes a crystal to amorphous structural transition triggered by an elastic shear instability [11]. The critical pressure observed in the molecular dynamics simulation again was that predicted by finite-load stability criteria. By manipulating the potential model, it was possible to explain why in $\beta - SiC$ the lattice disorders at the threshold of instability, whereas in diamond cubic Si, described by essentially the same Tersoff potential, the lattice undergoes a polymorphic transition to the tetragonal $\beta - Sn$ structure [12].

The study of <u>fracture toughness</u> is the ultimate goal of this project. We intend to determine through simulation the critical stress intensity factor necessary to cause an existing crack to propagate in the interfacial system. Molecular dynamics studies of crack tip extension in crystalline lattices have been carried out over a number of years. Most studies were concerned with the determination of brittle or ductile behavior including the brittle-to-ductile trasition [13]. More recently, very large scale simulations using millions of atoms have been reported, revealing the onset of a dynamic instability when the crack speed reaches a certain threshold, about one third of the Rayleigh speed [14]. The behavior of the crack tip in the presence of an interface is expected to be even more complicated than what has been studied thus far. It appears that molecular dynamics will not be able to go to sufficiently large systems or long enough times to realistically represent both the interface and crack. A hybrid method which links molecular dynamics with simulations at the mesoscopic level is needed in order to properly address the issue of modeling fracture toughness. The development of a multiscale approach is very much a problem of current interest [15].

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MULTISCALE MODELING OF MICROSTRUCTURE IN SIC FIBERS: BRIDGING THE GAP BETWEEN SIMULATIONS AND EXPERIMENTS

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Abstract

The aim of this project is to develop an atomistic approach to modeling the high-temperature strength of SiC fibers in ceramic-matrix composites. There exists much current interest in applying multiscale modeling techniques, in the sense of theory and simulation across length scales spanning angstroms to microns and beyond, to technologically relevant problems of a grand-challenge nature. Considerable capabilities for calculating and even predicting fundamental materials properties and behavior are now available; however, with few exceptions they have not been focused on revealing how specific microstructures evolve in an environment of elevated temperature and stress. From the experimental side, there also exists a need to better understand the factors which govern thermomechanical properties under controlled conditions. By developing a robust model, based on a realistic description of the interatomic interactions and integrated simulation techniques of molecular dynamics and kinetic Monte Carlo, and applying it to analyze various microstructural features of a SiC fiber, we intend to demonstrate a level of synergy between simulation and experiment where modeling results on material strength can be combined with benchmark measurements on well-characterized specimens to obtain greater insights than is feasible with either approach alone.

Interatomic Interaction Descriptions

The issue of having an interatomic potential which is sufficiently realistic for the quantitative analysis of microstructure of a binary compound such as SiC is crucial to the successful development of a robust model for atomistic and mesoscale simulations. We have thus adopted the empirical bond-order potential, a purely covalent model, developed by Tersoff [1], and have studied the physical properties of beta-SiC (3C) using this description. Since the original Tersoff model was developed for Si, we have used it to study thermodynamic properties [2] and the Grüneisen parameter [3]. Our SiC results now include equation of state, cohesive energy, elastic constants, and surface relaxations [4], as well as lattice vibration, heat capacity, thermal expansion [5], and thermal conductivity [6], all for a perfect crystal. In addition, we have shown that while point defects have little effects on thermal properties, they have dramatic influence on the thermal conductivity [6]. Fig. 1 shows the predicted thermal conductivity values, obtained using the Green-Kubo expression from linear response theory, are in reasonable agreement with experiment for temperatures above one third the Debye temperature (1200 K). Fig. 2 shows the local density of states calculated using a new Order-N method which we have developed [7]. The improved computational efficiency will enhance our ability to probe the vibrational behavior of local defects.

The fact that the Tersoff model completely ignores the effects of charge transfer means that certain properties of SiC will not treated properly. For example, we already know that in the phonon dispersion curves the optical branches are not described correctly in the vicinity of center of the Brillouin zone [5]. Given that SiC is known to be about 12% ionic, we feel it is important for the next phase of our model development to incorporate the electrostatic interaction effects. Rather than constructing an empirical model such as those proposed for compounds such as SiO_2 [8], we have embarked on the development of a tight-binding (TB) description in a collaboration with colleagues at the Ames

Laboratory [9]. Our approach is to exploit the considerable experience derived from building TB models for Si which includes the use of an environment-dependent term for the short-range repulsive part of the Hamiltonian, as well as fitting the TB parameters to a database of ab initio calculations.
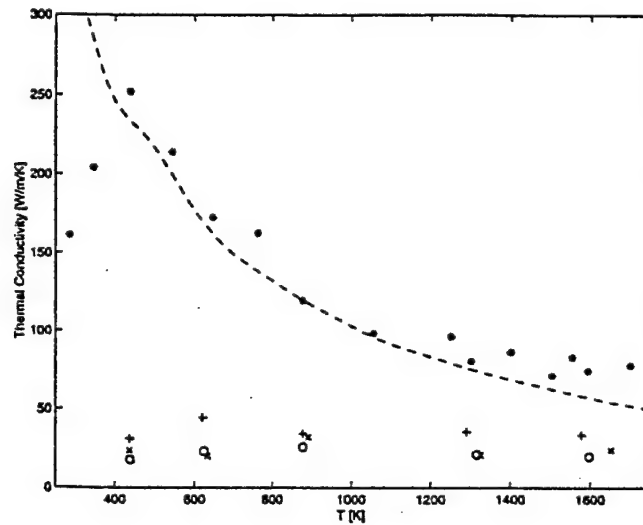

Figure 1: Comparison of calculated thermal conductivity (asterisk) of perfect crystal SiC (3C) with measurements (dotted curve). Other symbols denote the effects of various point defects at a concentration of 0.5%.
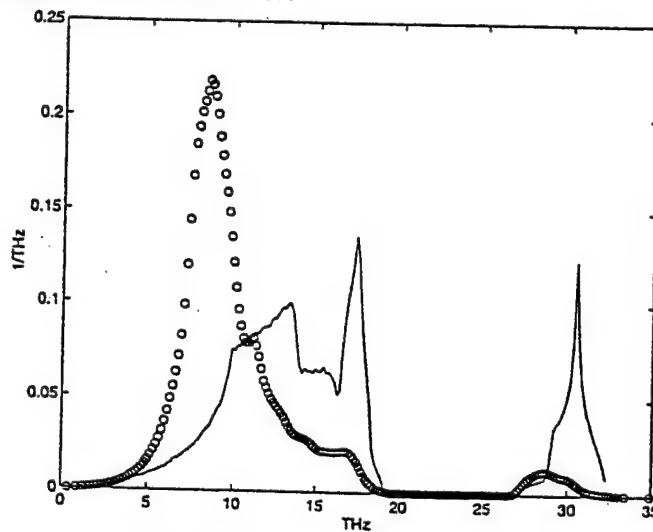

Figure 2: Local density of vibrational states (circles) of a Si atom adjacent to a C vacancy in SiC (3C). Also shown are the density of states (solid lines) of the Si atom in the absence of the C vacancy (perfect 3C lattice).

Present progress is that a database consisting of band structure, electronic density of states, cohesive energy curves and charge density plots has been generated using DFT-LDA method for the diamond, 3C, 2H, CsCl, and NiAs structures of SiC lattice. There are 21 TB parameters for the electronic band structure, and 15 parameters for the repulsive terms. Total energy fitting for Si:C composition of 1:1 has an average error of about 0.2 eV. We expect that our approach will result in a more robust description than the existing TB models for SiC [10,11].

Structural Phase Models

Our studies have been concerned thus far mostly with the beta-phase (3C) of SiC. Some preliminary calculations have been made for the alpha-phase (4H). Note that because the Tersoff potential only extends to second neighbors, energetically it does not distinguish between equilibrium 3C and 4H phases. However, the two phases will have distinct dynamical and transport properties, for example, the local density of states and the thermal conductivity for 4H should show an anisotropy relative to the basal plane. We have previously shown that the Tersoff model gives rather good results for elastic constants for the 3C structure. Now that measurements for 4H and 6H have just appeared in the literature [12] we are in the process of testing the potential against these results.

Limited studies of symmetric twist grain boundary structure using the Tersoff potential have been made to obtain relaxed atomic configurqations corresponding energies and elastic constants [13]. Since grain boundaries are of central interest in our project we intend to pursue this investigation in a more systematic fashion once our TB model is developed. There are important issues concerning the behavior of polar versus nonpolar interfaces which have been addressed by Kohyama using first-principles calculation [14]. These results provide an excellent basis for validating our TB model which is considerably less intensive computationally. Computational efficiency is an important issue because in microstructural evolution one needs to consider simulations for large systems (number of atoms) as well over long period of time. For this reason, first-principles methods, despite their accuracy, are not suitable for studying microstructure-property relations in a system such as SiC.

Stoichiometry

An appropriate SiC-based fiber for our model formulation is a high-strength, fine-diameter specimen derived from organosilicon polymer with low oxygen content [15]. However, these fibers still contain a significant amount of excess carbon, typically Si wt % is 55-63 as compared to 70 wt % for stoichiometric SiC. To study the effect of stoichiometry on fiber microstructure and properties we will construct atomistic models of Si_xC_{1-x} (x = 0.5 to 0.34) to determine sensitivity of calculated properties to stoichiometric ratio. Preliminary results, Fig. 3, show a general decrease of strength with increasing temperature and increasing strength with increasing C/Si ratio above 1.0 .
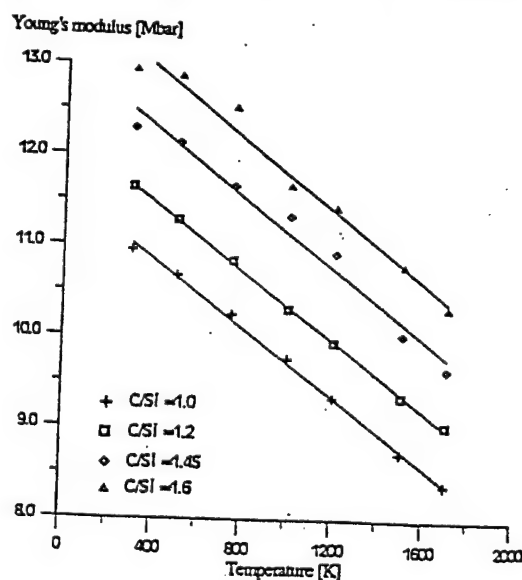

Figure 3. Effects of stoichiometry on Young's modulus of SiC (3C) calculated using the Tersoff potential model. Solid lines show linear temperature regressions.

SiC/SiO$_2$ Interface

In the oxidation of SiC, a layer of SiO$_2$ forms over the SiC. This is a significant microstructural detail which means that on the scale of atomistic simulation, one needs to understand the structural and mechanical behavior of a c-SiC/a-SiO$_2$ interface. We will begin the study of such interfaces by building a capability to simulate bulk SiO$_2$ first. For this work we will adopt a pair potential derived by fitting to ab initio calculations on small clusters [8]. Agreement between the elastic constants calculated using this potential is comparable to what we have found SiC.

Grain Size Effects

While grain size distribution is controlled primarily by the conditions of heat treatment, Si:C ratio also can have an effect. The presence of excess C will limit grain growth; high C content will result in grain sizes in the range several to tens nm, whereas without excess C rapid grain growth up a micron size can be expected. Simulation is particularly useful to elucidate how grain size distributions affect the thermomechanical properties, since experiments have difficulties in isolating the different effects of specific microstructural features. Monte Carlo techniques have been applied to study microstructure evolution in 2- and 3-D problems [16]. This may be regarded as a mesoscale approach. In the context of multiscale modeling, it is necessary to link such calculations to atomistic simulations based on interatomic potentials in order to make the results quantitative and predictive. Recently, the feasibility of a micro-meso connection has been demonstrated in revealing the atomistic mechanism of dislocation junction formation and destruction [17]. Just as the linking of molecular dynamics to dislocation dynamics allows one to predict stress-strain behavior in specimens of micron size, one can expect to couple molecular dynamics to Monte Carlo to study the behavior of polycrystal deformation with grains of micron size.

Another relevant recent development is the direct simulation of nanocrystals with grain sizes in the nm region [18, 19]. These studies show that certain microstructural processes are now within the range of simulation capabilities, behavior such as a reverse Hall-Petch effect [19, 20] and Coble creep [21].

Elastic Stiffness

We envisage that once suitable microstructure models of SiC fiber are developed, we can carry out atomistic and mesoscale calculations to investigate how the system behaves under conditions of high temperature and applied load. We have previously considered such behavior in a simpler system, a homogeneous lattice (a crystal without microstructure), and showed that the elastic deformation response of the lattice can be fully described in terms of the so-called elastic stiffness coefficients which are essentially the generalization of elastic constants to finite strain [22]. The stiffness coefficients are well defined at arbitrary strain, they can be evaluated by atomistic simulation, and they are sufficient in predicting the critical stress at which a structural instability will set in. We will extend the derivation of these coefficients to a polycrystalline lattice in order to understand atomic mechanisms of deformation at interfaces. It has been revealed in recent simulation of deformation of nanocrystals that interfacial sliding is an important mode of deformation [19, 20].

Acknowledgment/Disclaimer

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ATOMISTIC MODELING OF THERMAL AND MECHANICAL BEHAVIOR OF SIC AND SIO$_2$

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Introduction

A major goal of this project is to probe the high-temperature strength and deformation behavior of SiC through atomistic simulations. Besides contributing to the general development of multiscale approaches to modeling thermomechanical response of crystalline solids [1], our work is focused on providing results that will be useful in analyzing and interpreting on-going experimental efforts to produce SiC-based fibers with improved thermomechanical properties [2]. To achieve this goal, we are adopting a three-step strategy. First, we demonstrate that the interatomic potential for SiC we are using gives sufficiently realistic thermal and mechanical properties, such as the thermal expansion and conductivity, and the elastic moduli. Secondly, we carry out simulations of mechanical deformation as a means of determining the theoretical (ideal) strengths of the model SiC, using single-crystal structure initially before going on to study amorphous and nanocrystalline structures. Lastly, we consider crack-tip responses and fracture at high temperature in the presence of various microstructural features.

We have also begun similar investigations on SiO$_2$, a generally important ceramic material component which is invariably present as a coating on SiC fibers. We are again concerned with modeling the thermal and mechanical properties in single-crystal and amorphous phases using an appropriate interatomic potential model. Once these are determined, we will then investigate SiC/SiO$_2$ interfaces and focus on thermal transport, strength and mechanical deformation. By integrating these results with the above studies of microstructural effects on SiC, we expect to obtain the necessary insights toward a better understanding of the dominant factors controlling the high-temperature strength and fracture toughness of SiC fibers.

Interatomic Interaction Descriptions

We have made rather extensive use of an empirical bond-order type potential model, originally developed by J. Tersoff [3], to calculate various physical properties of $\beta - SiC$ (3C). These include equation of state, cohesive energy, elastic constants, and surface relaxations [4], as well as lattice vibration, heat capacity, thermal expansion [5], and thermal conductivity [6]. Comparisons with available experimental data, some of which are shown in Table I [4], indicate reasonable agreement. The same also can be said in using the Tersoff potential to predict thermal properties [5,6]. Table I shows that the Tersoff potential is superior to two other potential models, Pearson and MEAM which have not been tested as extensively. The results denoted by TB are a limited calculation using the tight-binding approximation [7]; this work is not being continued. Although the Tersoff potential has been reasonably successful, it is clear that considering only the covalent nature of the chemical bonding and ignoring completely the ionic interactions is a serious drawback. Given that SiC is known to be abut 12% ionic, the neglect of

charge-transfer effects means that properties which are governed by long-range interactions, such as zone-center optical modes, may not be described properly.

Table I. Simulated and experimental properties of $\beta - SiC$ (3C) [4].

		Tersoff	Pearson	MEAM	TB	Exp't
lattice parameter a	[A]	4.32	4.19	4.2	4.36	4.36
cohesive energy E	[eV]	-6.18	-7.71	-6.4		-6.34
bulk modulus B	[GPa]	225	990	211	229	225
C_{11}	[GPa]	436	1095		372	390
C_{12}	[GPa]	120	937		157	142
C_{44}	[GPa]	255	606	205	256	256
da/dT	[10^{-6} nm/K]	2.5				1.4
dC_{11}/dT	[GPa/C]	-0.036				-0.025
dC_{12}/dT		-0.0046				-0.011
dC_{44}/dT		-0.038				-0.007
dB/dP		4.1				2.9/4.0
γ_s(111)	[erg/cm^2]	2525				2180

We have embarked on a systematic development [8] of a tight-binding model (TB) for SiC, a simplified electronic structure approach in which electronic wave functions are expanded in a small set of a and p local orbitals. The procedure we follow is to fit the Hamiltonian model parameters to a database of first principles calculations based on density-functional theory with local density approximation (LDA), and introduce an environment-dependent term for the short-range repulsive part of the interaction [9]. This approach has been recently applied to pure C and Si in studies of point defects, lattice anharmonicity, liquid and amorphous systems, C_{60} and Si 7x7 surface reconstructions, and low-energy Si clusters, all demonstrating good transferability. Its most distinctive feature is that all interactions are coordination number dependent, and are explicitly screened. For our SiC TB model, a comprehensive property database has been generated for six bulk phases, 3C-SiC (zinc-blend), 2H-SiC (wurzite), NaCl structure, NiAs structure, anti-NiAs structure, CsCl structure, in addition to pure Si and C, and 25% and 75% stoichiometry. The properties include electronic band structures, cohesive energy-volume curves, elastic constants, frozen phonon energies, and point defect configurations and formation energies. Fitting of the TB model parameters to the family of target properties is carried out using nonlinear optimization and/or simulated annealing algorithms. Although the model development is still on-going, candidate models have been obtained which can reproduce the target properties on a level that is much better than the Tersoff empirical potential. The accuracy of the TB model relative to LDA results are shown in Tables II, III, and IV for the bulk 3C properties, point defect formation energies (C-rich), and energy differences between phase minima, respectively.

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Table II. Equilibrium 3C-SiC properties.

Target	LDA	TB (rel. error, %)
a [A]	4.34	2.2
E [eV]	-6.34	-3.8
B [GPa]	224.6	-1.8
C11 - C12 [GPa]	264	-10.5
C_{44}^{o} [GPa]	273.3	-8.4
$TO(\Gamma)$ [meV]	97.9	10.7
$LO(\Gamma)$	97.9	same
$LA(X)$	78.3	6.9
$LO(X)$	103.8	-5.1
$TA(X)$	46.0	-1.4
$TO(X)$	94.8	-2.9

Table III. Defect formation energies (C-rich).

Target	LDA	TB (rel. error, %)
V_{Si} [eV]	7.0	5.4
V_C	3.9	-3.1
Si_C	6.4	-6.2
C_{Si}	3.4	10.7

Table IV. Phase minima energy differences.

Target	LDA	TB (rel. error, %)
2H-3C [meV]	12.2	293
NaCl-3C	686.9	0.0
NiAs-NaCl	106.8	-5.3
NiAs-aNiAs	554.0	11.8
aNiAs-CsCl	873.0	-2.9

The potential model for SiO_2 we have adopted is a force field developed by combining ab initio calculations on small cluster and macroscopic information from experimental data [10]. The potential consists of a Coulombic term and a covalent short-range interaction in the Buckingham form, with a single free parameter, the effective charge of Si. This description has been shown to combine accuracy and transferability to other polymorphs, while its applicability for probing thermal and mechanical properties remains to be tested. Additionally, electronic-structure information on amorphous silica [11] is now available for validation studies.

Thermal Conductivity

Given that our focus is on mechanical behavior at high temperatures, it is appropriate to ensure that our understanding and modeling capabilities extend to thermal responses, specifically thermal expansion and conductivity, and how they will be affected by various specific microstructural variables. We have recently demonstrated that molecular dynamics simulations, with an input of a reasonably realistic interatomic potential, provide an effective means of dealing with thermal behavior of materials [5,6]. Using a statistical-mechanical method based on linear response theory, we have calculated the thermal conductivity as a dynamic quantity through the determination of heat current correlation function, and obtained results for SiC in quite good agreement with experiments in the temperature range 400 - 1700 K. It is noteworthy that our predicted effects of point defects as giving rise to a marked reduction of conductivity and a loss of temperature dependence are in accord with observations, as is our prediction that point defects have essentially no effect on the thermal expansion. Using the Tersoff potential we also find the conductivity of amorphous SiC to be an order of magnitude lower in value than that for a high concentration of point defects, with an increasing variation with temperature that is characteristic of amorphous materials.

We have made further progress in extending the above method of thermal conductivity calculation based on classical mechanics to lower temperatures where quantum effects begin to play a role. We have developed a quasi-momentum relaxation method to treat the contributions from the so-called Umklapp process which give rise to an exponential temperature dependence in contrast to an algebraic behavior associated with the normal processes of phonon scattering. A significant improvement is found in describing the observed thermal conductivities of Si and C, whereas the effects in SiC are relatively small [12]. Although this enables classical molecular dynamics simulation to reach the temperature range, $T_D/4 < T < T_D$, where T_D is the Debye temperature, the very low temperature region, where specimen size effects are also controlling, is still not accessible to our method without fundamental modifications. Fortunately, this is not a practical limitation since we are primarily interested in high-temperature properties and behavior.

We are presently in the process of applying our method to calculate the thermal expansion and conductivity of crystalline (quartz and cristobalite) and amorphous SiO_2 structures. Comparison of results with experiments will provide further validation of the potential model [10].

Strength Determination

Recently we have shown that in predicting the critical strain at which a stressed lattice becomes structurally unstable, the applied stress must appear explicitly in the conditions of instability [13, 14]. This result stands in contrast to the well-known stability criteria, generally attributed to M. Born, where the effects of applied stress enter only through the elastic constants C_{ij}. For a cubic lattice under an applied hydrostatic stress, the load-dependent instability conditions are

$$B = (C_{11} + 2C_{12} + P)/3 > 0, \quad G' = (C_{11} - C_{12} - 2P)/2 > 0, \quad G = C_{44} - P > 0$$

where P is positive (negative) for compression (tension), and the elastic constants are to be evaluated at the current state. A number of direct simulation studies have shown that these criteria do accurately describe the critical value of P at which the homogeneous lattice becomes unstable. One may therefore regard P_c as a definition of theoretical or ideal tensile strength of the lattice.

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We have performed a series of molecular dynamics simulations of $\beta - SiC$ (3C) under hydrostatic tension using the Tersoff potential model discussed above [15]. The system response, observed at 300 K, showed that at $P_c = 37.0$ GPa the violation of condition B > 0 (spinodal instability) was accompanied locally by decohesion on {111} shuffle planes. The spontaneous nucleation of cracking, initiation of brittle fracture on the atomistic scale (simulation cell contained N = 216 atoms with periodic boundary conditions), is not unexpected given that SiC is considered an inherently brittle material. We have further analyzed the simulation results by developing a site-dependent measure of the temporal evolution of the lattice instability [16]. We find the crack nucleation process to consist of the onset of local instabilities at several distinct sites in the system, followed by coalescence of these instabilities which then triggers bond rupturing along a plane. Once decohesion starts atomic relaxation on the newly generated cracked surfaces appears to take place immediately on a microscopic time scale. Based on these results we conclude that under hydrostatic loading the theoretical tensile strength of our model SiC is $\sigma_{ten} = 37$ GPa, with an associated critical strain of $\varepsilon_{ten} = 0.153$ [15]. For comparison we note that under hydrostatic compression a similar simulation using the same SiC potential model one finds a structural instability at $\sigma_{comp} = 714$ GPa and $\varepsilon_{comp} = 0.225$ at 300 K, or $\sigma_{comp} = 1156$ GPa and $\varepsilon_{comp} = 0.266$ at 0 K, showing a remarkable stiffness and a significant temperature variation [17]. In contrast to crack nucleation, the structural response to compression is a crystal to amorphous transformation which may be traced to chemical disordering effects due to atomic size difference in the SiC lattice. Relative to the above stability criteria, the elastic deformation mode associated with instability under compression is G = 0. It is interesting to recall that in a simulation of hydrostatic compression of diamond-cubic Si, using the same kind of bond order potential, a polymorphic transition to beta-tin structure was observed at $\sigma_{comp} = 111$ GPa and $\varepsilon_{comp} = 0.14$ upon violation of G' = 0 [18].

Fracture, Interfacial Deformation and Plasticity

The fore-going simulations of material strength, carried out on a single-crystal specimen of model SiC, are being extended to amorphous and various interfacial structures to further explore the interplay between elastic and plastic processes of deformation. We envisage systematically introducing increasing degrees of microstructural complexity through specimens of bicrystals and polycrystals (actually nanocrystals because of the constraints of atomistic simulation). We also plan to investigate crack-tip deformation in the materials of interest, progressing from single crystal fracture in SiC and fracture of amorphous SiO_2 to debonding at a SiC/SiO_2 interface. In contrast to tensile strength, the determination of fracture toughness, the amount of energy needed to break a piece of material in the presence of realistic microstructure, is quite a challenge for atomistic simulation. For a brittle material it can be measured as the energy absorbed per unit area of crack, G, or in engineering ceramics it is defined as $(EG)1/2$, with E being the Young's modulus. A related quantity, which is well defined and more amenable to direct simulation, is the work of adhesion W_{ad}, the energy required to separate reversibly the two sides of the interface [19]. This quantity is known to scale with the fracture toughness if a crack propagates along the interface in a cleavage manner [20]; for this reason W_{ad} is also called intrinsic fracture toughness. Experimentally, W_{ad} is difficult to measure because of the influence of chemical and structural defects at the interface. We will undertake to study this property to establish a correlation with various microstructural features. In a preliminary calculation of W_{ad} for a c/a SiC interface using the Tersoff potential, we obtained a value of 3.8 J/m^2. The only experimental result

available for comparison is an estimate of 3.28 J/m^2 for SiC coating/pitch 55 carbon interface [20].

We anticipate that simulations of deformation of nanocrystals over a range of temperature could provide new insights into the role of grain boundary sliding in local stress relaxation. Of interest here is the competition between dislocation-like plastic deformation within a grain and intergranular slip [21]. Plastic deformation leading to a reverse Hall-Petch effect, the flow stress decreasing with decreasing grain size, has been reported in a recent molecular dynamics simulation of model fcc metal in nanocrystalline phase [22]. By working at high temperature with nanometer size grains, it appears that one is now able to probe Coble creep [23]. These developments, along with the prospect of linking atomistic simulation with mesoscale methods such as finite-element analysis [24], should allow us to better understand how to optimize the thermomechanical properties of SiC fibers for high-temperature applications.

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